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Charles V. Clemency

Principal Investigator

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The low temperature dissolution kinetics of several rock-forming minerals is described, rate constants calculated, and implication of the results on interpreting mechanisms discussed. Minerals studied include: brucite, antigorite, phlogopite, talc, muscovite and some feldspars. Two different experimental methods were used, an older CO_2 method and a new method using ion exchange resins as a trap for released ions. Using this new method, increases in dissolu-		

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tion rate of up to about 70 times were obtained, allowing better resolution of the long-term kinetics. The resin method simulates dissolution in nature approaching an open system, whereas, in contrast, the older CO_2 method simulates dissolution in a closed system of weathering conditions. In an open weathering system, rainfall would be high and drainage good, whereas in a closed system, rainfall would be low and drainage poor.

The sequence of magnesium-bearing minerals brucite, antigorite, phlogopite, and talc illustrate a series of layer- or sheet-type structures of increasing chemical and structural complexity. Experiments showed that the dissolution rates of these minerals in the order: brucite > antigorite > phlogopite > talc if surface areas and pH are the same. Except for brucite, all these minerals dissolve incongruently, with Mg being released from the octahedral sheets more rapidly than Si is released from the tetrahedral sheets. The more tetrahedral Si sheets present in the structure, the less soluble is the mineral. The dissolution kinetics of layer-type silicate minerals appears to be related to or controlled by the rate of destruction of the tetrahedral silica sheets of the mineral. This is probably related to the strong nature of the Si-O bonds and the greater energy necessary to break them.

Resin experiments do not support presence of the hypothetical "protective layer" suggested by some workers because initial rates appear linear rather than parabolic when using this method. Resin experiments were done using phlogopite, but an experiment is still underway using a special cell containing both a cation and an anion exchange resin and using a feldspar (oligoclase) as the mineral of interest. Results of this experiment will be published upon completion.

Another line of investigation was pursued simultaneously with the foregoing. An attempt was made to study the chemical composition of the surface of leached mineral fragments using the techniques of x-ray photoelectron spectroscopy (ESCA) and Auger electron spectroscopy (AES). ESCA studies of four leached feldspars of different compositions were unsuccessful because of the presence of perthitic intergrowths which confused the picture. AES studies of phlogopite cleavage surfaces was more successful. The chemical composition of the surfaces of both leached and unleached phlogopite was studied by AES. A definite depletion of K was observed in the leached specimens compared to unleached material. Other ions present (Mg, Al, Si, and F) showed no detectable differences in concentration. Upon standing for three months, K content of the leached surface was observed to increase, indicating a migration or diffusion of ions towards the surface from within the structure. Lack of funds prevented a long-term study to measure actual diffusion rates over time.

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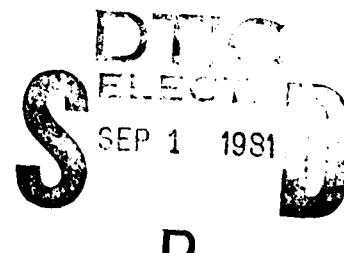


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LIST OF PARTICIPATING SCIENTIFIC PERSONNEL

<u>Name</u>	<u>Degree Received</u>	<u>Date of Degree</u>
Patricia M. Costanzo	M.S.	1981
Feng-Chih Lin	Ph.D.	1981

INTRODUCTION

The objective of this study was to provide new, accurate experimental data on the low temperature dissolution rates and kinetics of some common rock-forming minerals for which such data are currently lacking or inadequate. These data are important and useful in calculating thermodynamic equilibrium and dissolution rate constants, constructing mineral equilibria diagrams, and deriving kinetic equations upon which we base our ideas and create conceptual models to explain rock weathering, clay mineral genesis, composition of ground water constituents, and other natural processes that take place at the low temperatures and pressures found at the earth's surface. Because these natural processes are so complex, theoretical geo-chemists must largely base their mathematical models and concepts on experimental data obtained on simple systems such as were undertaken in this study. Serious problems present themselves in conducting experiments of this nature, however, that result in few attempting this type of work. For example, chemical reactions between "insoluble" silicate minerals and natural solutions at low temperature are very slow, and long periods of time (many weeks, months or years) are required. In addition, sophisticated techniques and apparatus are necessary for maintaining constant temperature and pH during the experiment and for the analysis of the extremely dilute solutions that result. Tedious and numerous chemical analyses at the lowest limitations of detection require patience, a high degree of analytical skill and a lot of time. The typical experiment requires 6-10 months for completion. It is no accident that few care to pursue such studies.

In table I are listed the talks resulting from this study which were presented at national and international scientific meetings. In table II are listed four journal articles already published (1-4), two which have been submitted and are now in review (5-6), and two tentative titles of experiments still in progress (7-8), and title of a paper (9) which will be submitted for publication at the time it is presented at the International Clay Conference in Italy in September 1981. Each of the papers in table II has been numbered and will be referred to by these numbers in the discussions which follow. Other references are listed in the bibliography in the usual manner.

DISSOLUTION STUDIES USING THE CO₂ METHOD

This grant supported a continuation of previous work concerning the dissolution kinetics of eight feldspars of different compositions using an experimental technique which will be referred to as "the CO₂ method" in the following discussion. A full description of this technique, chemical data on these eight feldspars, and other relevant data and information which form the basis and background of the present study may be found in Busenberg and Clemency (1976). In brief, the CO₂ method involves the dissolution of a finely-ground mineral powder (5% by weight) in one liter of distilled water contained in a closed polyethylene reaction cell through which is bubbled CO₂ at one atmosphere pressure. Aliquot samples are withdrawn periodically and analyzed for dissolved constituents. In contrast to the CO₂ method, the "resin method" will be discussed also. It is described below.

Table I. List of papers presented at national and international meetings as a result of this study.

1. F.C. Lin and C.V. Clemency (1979). Kinetics of dissolution of phlogopite mica at 25°C and 1 atm CO₂. Abstracts, 28th Annual Clay Minerals Conference, Macon, Georgia, p. 31.
2. C.V. Clemency and F.C. Lin (1979). Dissolution kinetics of phlogopite using ion exchange resins. Abstracts, 28th Annual Clay Minerals Conference, Macon, Georgia, p. 32.
3. F.C. Lin and C.V. Clemency (1980). The dissolution kinetics of brucite, antigorite, talc and phlogopite at room temperature and pressure. Abstracts, 29th Annual Clay Minerals Conference, Waco, Texas, p. 65.
4. F.C. Lin and C.V. Clemency (1980). The kinetics of dissolution of muscovites at 25°C and 1 atm CO₂ partial pressure. Abstracts, Proceedings of the 3rd International Symposium on Water-Rock Interaction, Edmonton, Canada, p. 69-71.
5. C.V. Clemency and F.C. Lin (1981). The dissolution of clays. Accepted for presentation at the 7th International Clay Conference, Bologna, Italy, September 1981.

Table II. List of published journal articles, and incomplete reports resulting from this study, with reference numbers.

1. F.C. Lin and C.V. Clemency (1981). The kinetics of dissolution of muscovites at 25°C and 1 atm CO_2 partial pressure. *Geochim. et Cosmochim. Acta* 45, 571-576.
2. F.C. Lin and C. V. Clemency (1981). Dissolution kinetics of phlogopite.
 - I. Closed system. *Clays and Clay Minerals* 29, 101-106.
3. C.V. Clemency and F.C. Lin (1981). Dissolution kinetics of phlogopite.
 - II. Open system using an ion exchange resin. *Clays and Clay Minerals* 29, 197-112.
4. F.C. Lin and C.V. Clemency (1981). The dissolution kinetics of brucite, antigorite, talc and phlogopite at room temperature and pressure. *Amer. Mineralogist* 66, (to appear in July-August 1981 issue).
5. C.V. Clemency and F.C. Lin. The effect of the amount of cation exchange resin on the dissolution kinetics of phlogopite. (Submitted for publication to *Clays and Clay Minerals*, June 1981.)
6. C.V. Clemency and F.C. Lin. The dissolution of phlogopite using cation exchange resin enclosed by membrane. (Submitted for publication to *Clays and Clay Minerals*, July 1981.)
7. Dissolution kinetics of oligoclase using both a cation and an anion exchange resin. (Experiment still in progress)
8. Dissolution kinetics of phlogopite using both a cation and an anion exchange resin. (Experiment still in progress)
9. The dissolution mechanism of clays. (To be submitted September 1981)

Using the CO_2 method, dissolution studies were completed on two different muscovites (1), phlogopite (2), and on brucite, antigorite, and talc (4) in the early stages of this investigation. The four minerals brucite, antigorite, talc and phlogopite form a series of magnesium minerals with "sheet-type" structures of increasing chemical and structural complexity. An analogous series of aluminum minerals with similar sheet-like structures is formed by gibbsite, kaolinite, pyrophyllite and muscovite. Originally, both of these series were to be studied because they cover a large segment of the phyllosilicate family, and by progressing from simple to more complex compositions and structures, we believed that the mechanism of dissolution could be better understood. In addition, if results from one series could predict results from the other, the ideas generated would be considerably strengthened. Although the magnesium series of minerals were completed successfully, the aluminum series could not be completed. The reason was because any aluminum released from the minerals is almost immediately precipitated as amorphous $\text{Al}(\text{OH})_3$ which is very insoluble ($K_{\text{sp}} = 10^{-32}$). Thus, the release of aluminum could not be followed since the precipitated $\text{Al}(\text{OH})_3$ cannot be separated from the mineral in suspension in the reaction cell. For this reason, studies of the Al series had to be abandoned.

Results of the study on the magnesium series was published in (4). In summary, antigorite, talc and phlogopite were found to dissolve incongruently, i.e., Mg was released from the octahedral part of the sheets more rapidly than Si was released from the tetrahedral part of the sheets. The solubility of these layer-type minerals is apparently related to the

number of tetrahedral sheets present in the structure. In general, the dissolution kinetics of layer-type silicate minerals appears to be controlled by the rate of destruction (breaking) of the silicon-oxygen bonds in the structure. If surface areas and pH's are normalized for the four magnesium minerals, the order of solubility is: brucite > antigorite > phlogopite > talc. Full details, along with all data, curves and calculated rate constants may be found in publication (4). Reaction rate/solubility curves are summarized in figure 4.

DEVELOPMENT OF THE ION EXCHANGE RESIN METHOD OF DISSOLUTION

The difficulties encountered in studying the Al series of minerals described above led to thinking about ways to prevent precipitation of Al after it was released from the mineral and passed into solution. In addition, other workers (see references by Scott and Smith, 1966 and Hanway, 1957 given in 3) had found that traces of K^+ in solution had a large effect on the solubility of muscovite mica in water. This led us to the idea that dissolution rates may be strongly affected by the ionic strength of the dissolving medium, i.e., when mica dissolves and a small amount of K^+ goes into solution, that K^+ may have a large repressive effect on further dissolution of the mica. Perhaps if a cation exchange resin (H^+ form) were added to the mineral-water suspension, dissolution might be accelerated by adsorbing any released cations. The resin would not only act as a "sink" or scavenger for cations helping to keep the ionic strength low, but, in addition, would act as a source of H^+ ions

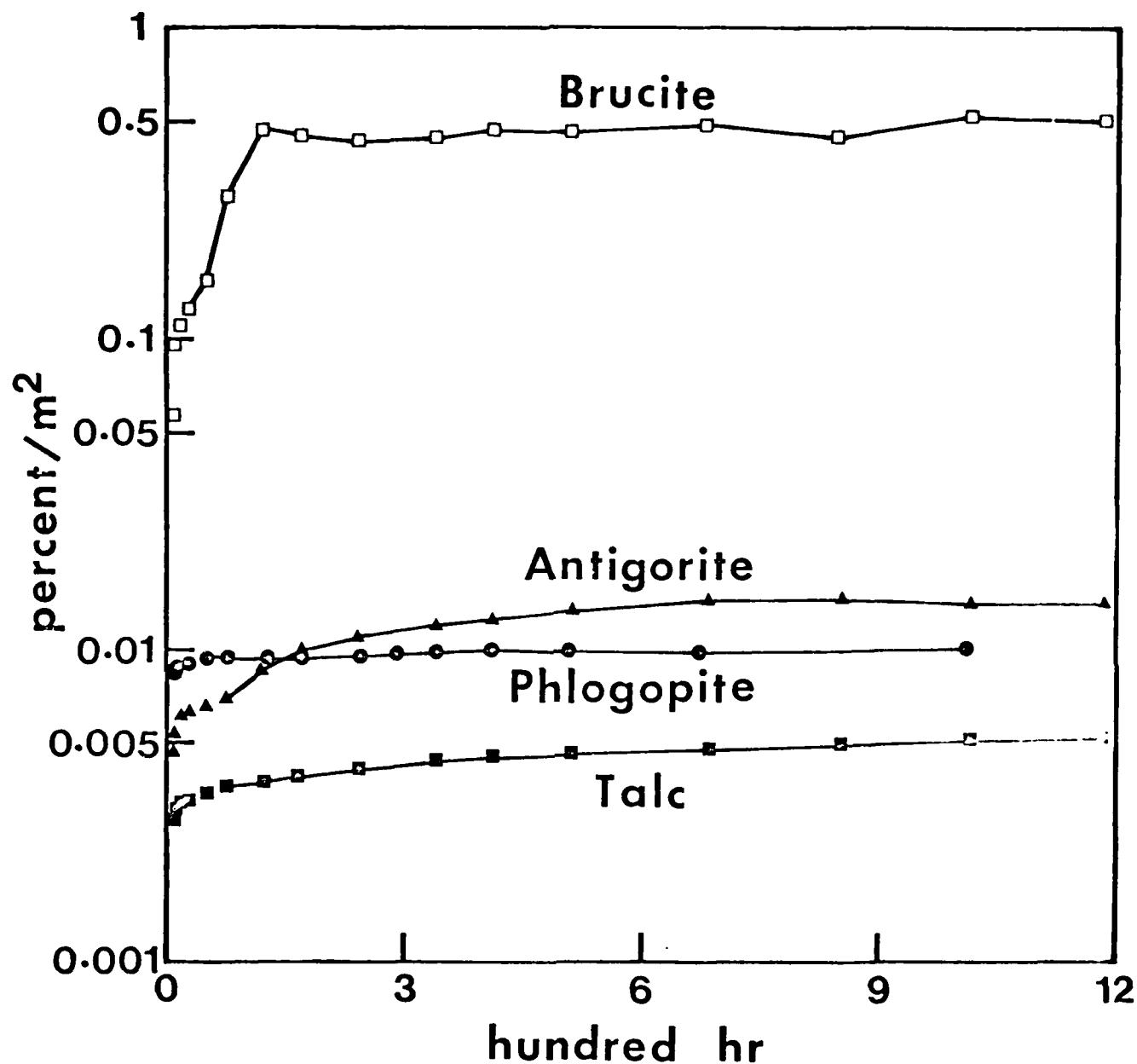


Figure 1. Reaction rate-solubility curves for brucite, antigorite, phlogopite and talc normalized in terms of weight percent mineral dissolved per square meter of surface area.

and serve as a buffer to maintain pH constant. The concentration of Al^{+3} would be kept low by immediate adsorption onto the resin so that the solubility product of $\text{Al}(\text{OH})_3$ would not be exceeded.

Phlogopite was chosen for our first cation exchange experiments because we had just completed a study on phlogopite dissolution; thus, material was available, and its behavior in pure water was already known. After a few quick preliminary studies, a whole series of phlogopite-resin samples were prepared and run as described in detail in (3). In summary, ambiguities that arose from the nature of the CO_2 experiment were eliminated, and a much clearer picture of the process of dissolution became visible. Whereas about 0.5% of the phlogopite had dissolved after 1,000 hours of reaction time using the CO_2 method, 36% dissolved using the resin method, an increase of 67 times in reaction rate (see figure 2). We were able to see that the kinetics were not parabolic in the early stages after all, but linear. This meant that there was really no evidence or reason to invoke presence of an "amorphous", "protective" or "residual" layer as invoked by many workers. Comparative data, curves, dissolution constants and detailed discussion may be found in (3).

Doubling the resin-to-mineral ratio

A second experiment using double the resin-to-mineral ratio was run to assess the effects of using different amounts of resin. In the first experiment 0.25 g of mineral and 1 g of resin resulted in about 36% of the phlogopite dissolving after 1,000 hours (curve b in figure 2). Note that the curve is almost a straight line up to about 200 hours, after which

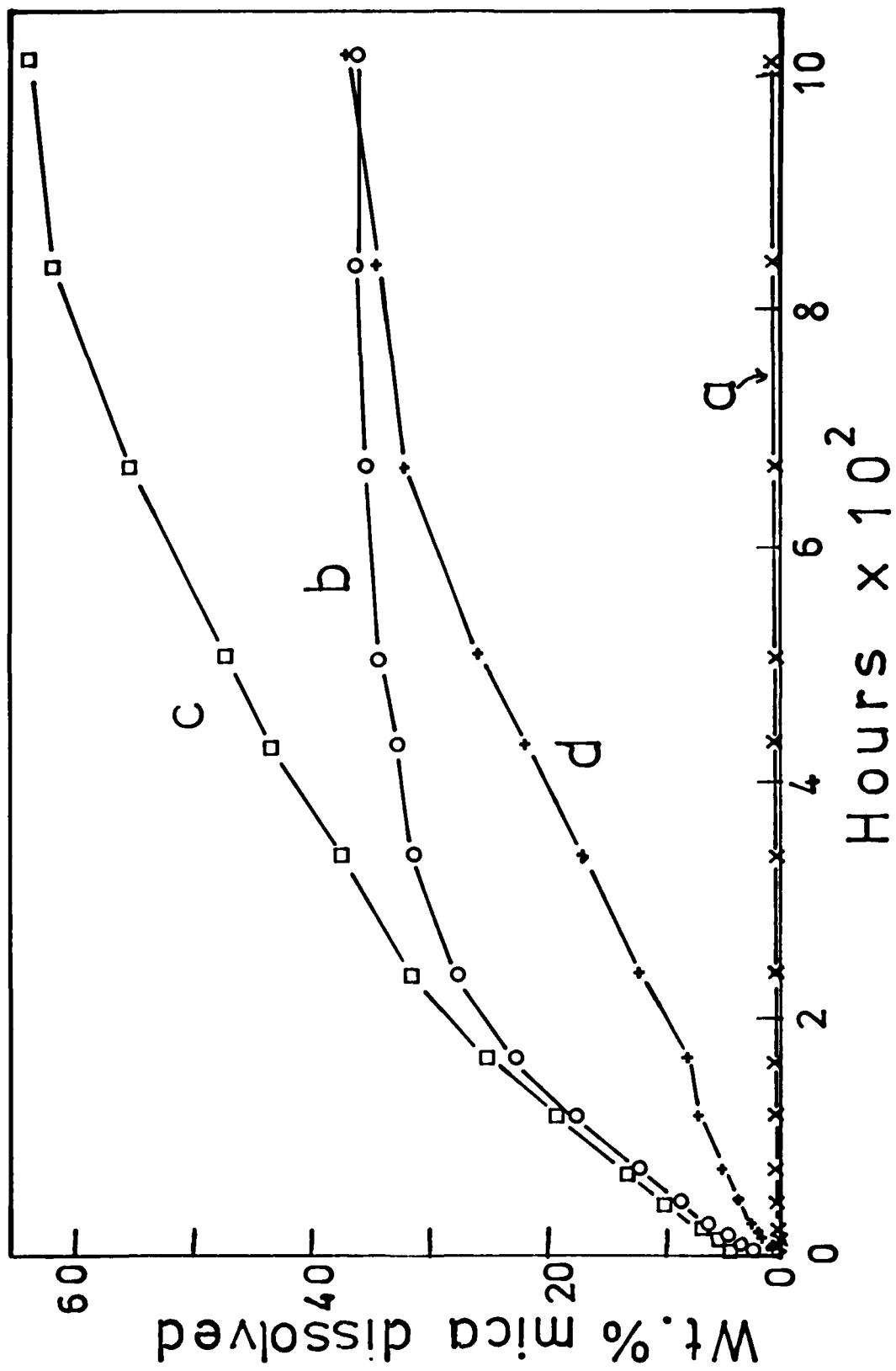


Figure 2. Dissolution rate curves for phlogopite: a) closed system using the CO_2 method, b) open system using 1g cation exchange resin in contact with 0.25g phlogopite, c) same as (b) except 2g of resin were used, d) same as (b) except resin was enclosed in a sack made of dialysis tubing.

the curve begins to flatten out (dissolution rate decreases). We attribute this departure from a straight line to the resin becoming saturated with dissolved ions and total surface area decreasing. The resin itself has a "distribution coefficient" which describes the equilibrium state of ions in solution and on the resin. As the percentage of the resin exchange positions occupied by metal ions increases, the ionic strength of the solution increases, repressing the rate of dissolution, and the curve begins to depart from a straight line.

Using 2 g of resin per 0.25 g of phlogopite, curve c of figure 2 was obtained. Results for the first 200 hours were essentially the same as for 1 g of resin. After 200 hours, however, curve c continues to rise at a rapid rate, eventually reaching about 63% completion. We again attribute the convexity of the curve to several possible causes:

1) H_3SiO_4^- and F^- , which are released from the mineral into solution as anions, also help to retard the dissolution rate, just as cations would do, 2) as the finer particles dissolve, the total surface area decreases lowering the amount of surface area exposed to solution, 3) resin exchange positions become increasingly saturated, resulting in an increase of ionic strength of the solution.

Using an anion exchange resin only

Since reducing the ionic strength of the cations in solution alone had produced a 67x increase in dissolution rate, we next wanted to study the effect of the anions released into solution on the dissolution rate. The anions released from this phlogopite were essentially fluoride and silicate

ions. Since these were not adsorbed by the cation resin, they accumulated in the solution as the mineral dissolved, possibly having a repressive effect on dissolution rate.

Another series of experiments was run using only an anion exchange resin in contact with the mineral particles, i.e., no membrane sack was used. The resin-to-mineral ratio was again 1 to 0.25. The results showed that almost the same amount of mineral dissolved as in pure water using the CO_2 method, i.e., about 0.6% by weight. Apparently the presence of anions in the solution does not have nearly the same repressive effects on dissolution as does the presence of cations. (Cations accumulated in the solution in this experiment just as they did in the CO_2 experiment.)

From these results we realized that maximum dissolution rate required the use of both cation and anion resins simultaneously. When both types are used in water purification, they are generally simply mixed together to form what is called a "mixed-bed" resin. However, we wanted to keep the resins separated so that each could be eluted of the ions it had adsorbed for analysis.

At the same time, we were cautioned by physical chemists that our high rate of dissolution may have been caused by actual contact of mineral grains with the resin. They suggested that although the pH of the bulk solution may have been about 4, the pH in the vicinity of the resin surface (the "double layer") may be much lower, producing an effect similar to adding strong acid to our solution.

Using a permeable membrane to separate resin from mineral

The dissolution experiment using 1 g of cation exchange resin and 0.25 of phlogopite in a test tube with 10 ml of distilled water as in (3) was repeated, except that the resin was enclosed in a small sack (fig.3) made of dialysis tubing (a permeable membrane). The pore size of this membrane was $40-80\text{\AA}$, large enough for cations to pass freely through, but small enough to prevent the mineral particles from direct contact with the resin. Results are given in detail in (6). In summary, initial reaction rates were reduced to about half, but the total amount of mineral dissolved after 1,000 hours was the same, 36%. In figure 2, curve d shows the dissolution curve obtained using this membrane technique. From the results we conclude that there is an increase in initial dissolution rate if the mineral particles are allowed to contact the very acidic resin particles. The total amount of mineral dissolved after 1,000 hours, however, is the same.

Use of cation and anion resins simultaneously

Another series of experiments was prepared using 1 g each of cation and anion exchange resin plus 0.25 g of mica and 10 ml distilled water. Each resin was enclosed in a separate sack made of dialysis tubing (see figure 3). Several attempts failed because, for some reason, when two sacks were present, they broke open spoiling the experiment. This problem was not encountered when only one sack was present. After many failures, a new type of reaction cell was designed (see figure 4) which worked well.

At this point we decided to use a plagioclase feldspar (oligoclase) in this experiment rather than phlogopite. This was because feldspar is a much more important rock-forming mineral than phlogopite and the results

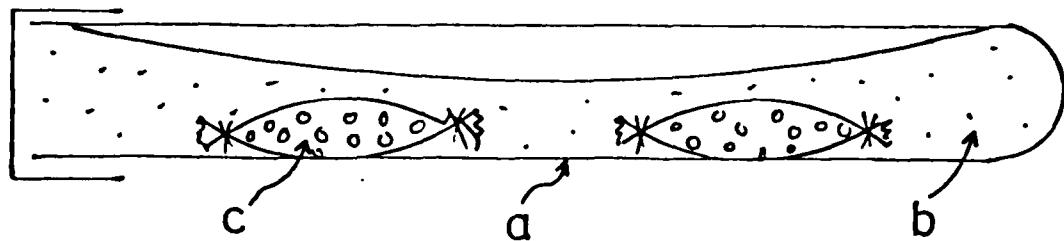


Figure 3. (a) Plastic test tube with cap (Falcon 3033) used in early experiments, (b) ten ml of distilled water plus 0.25 g of mineral, (c) sack made of dialysis membrane tubing containing 1.0 g of ion exchange resin and 1-2 ml distilled water. Sacks are tied with nylon thread.

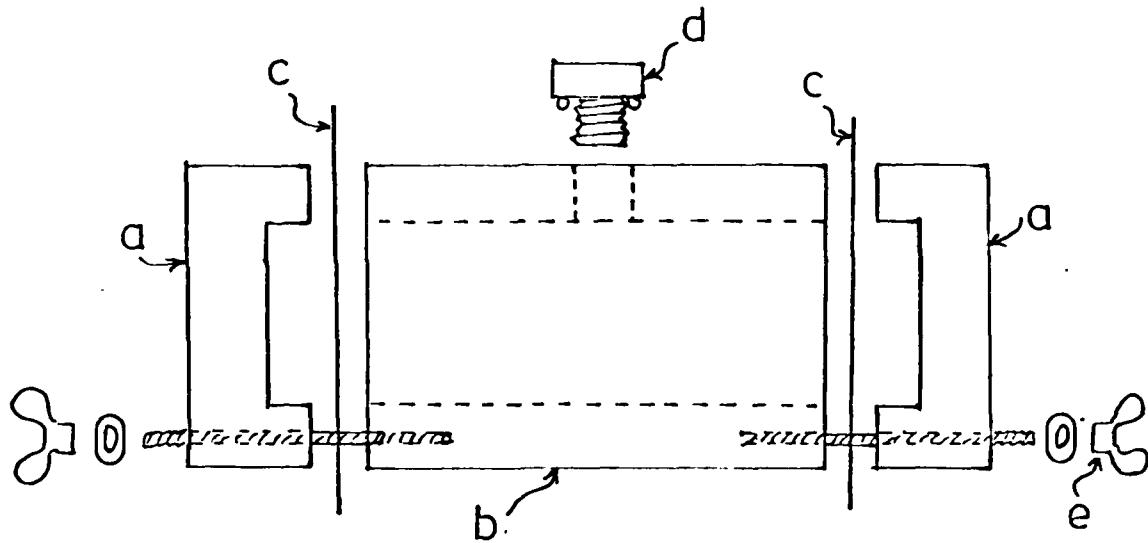


Figure 4. Three-chambered reaction cell made from 2" diameter plexiglass rod. Cell is about 3" long with a central hole of 1" diameter. End-caps (a) are about 7/8" long with a 1" diameter recess cut about 1/4" deep. Each end-cap contains a separate charge of either cation or anion resin plus enough distilled water to fill it. The central chamber (b) is about 2" long and has a threaded hole with a matching plug and "O"-ring through which a pH electrode can be inserted. The central chamber contains 10 ml of water and 0.25 g of mineral. The resin is separated from the mineral-water suspension by a sheet of dialysis membrane cut to fit. Parts of cell are held together by three 3/16" stainless steel rods (threaded and fitted with washers and wing-nuts) which are spaced 120° apart.

would have a much more general interest, and also because the phlogopite experiment was criticized by one reviewer who said that the large increase in dissolution rate may have been caused by the released F⁻ creating a substantial concentration of HF which caused the increase.

The experiment using both cation and anion resins along with oligoclase feldspar is still in progress as of this writing because it had to be re-run. Too late, we discovered after completing most of the work, that the anion resin had been contaminated with silica, probably during a preliminary NH₄OH wash. Evidently, the NH₄OH had dissolved considerable silica from the reagent bottle in which it was stored. This was a terrible blow because it is silica which is used to measure the dissolution rate of these minerals because it has the slowest release rate of all the ions, and therefore the most critical. Although we hope to recover some information from the failed experiment, it appears that the whole thing will have to be re-run. This will take many more months. It was at this point that the grant ended.

SURFACE ANALYSIS STUDIES

During the course of these experiments, we became interested in simultaneously pursuing another line of investigation, namely, trying to determine the nature or composition of the mineral surface remaining after dissolution in water. In the dissolution literature, much attention is given to this altered surface. Much of the early experimental work, such as that by Wollast (1967), Busenberg and Clemency (1976), and others, inferred a "parabolic stage" in the dissolution process. This was interpreted by these workers and theoreticians such as Helgeson (1971) and Paces (1973) as evidence of formation of an invisible, amorphous (?) "protective layer" or "residual layer" covering the surface of the mineral particles. Petrovic, et al. (1976) could find no directly visible evidence of such a layer using SEM and ESCA techniques. They concluded that if such a layer existed, it had to be of a thickness less than 10-20A.

Other new surface analysis techniques also became available at about this time called Auger electron spectroscopy (AES) and secondary ion mass spectrometry (SIMS) which claimed to be able to detect differences in surface layers as small as one atom thick.

We planned some experiments to seek evidence for (or against) the existence of this purported surface layer using these new techniques. We planned to compare the surface chemistry of fresh and leached (in water) mineral cleavage flakes using ESCA, AES and ISS/SIMS techniques. Two cleavage flakes of four different feldspars used in Busenberg and Clemency (1976) were prepared.

One flake was to be analyzed fresh (unleached), while the other was to be subjected to 1,000 hours of leaching in CO_2 -saturated water.

Dr. David Hercules of the University of Pittsburgh, an acknowledged leader in the field of surface analysis, was contacted and agreed to do the analytical work for us. In his laboratory, he had AES, ESCA and ISS/SIMS instruments available. Work was done over a two year period for us by Dr. Hercules.

Unfortunately, the results of all this work, although very promising, exciting and of apparently high potential, ended up as unclear and ambiguous data.

Although the whole story is too long and complicated to go into in detail here, a few highlights were as follows.

The first leached samples (the four feldspars) studied by Dr. Hercules were found to have their surfaces contaminated by some sort of "organic coating" which, according to him, rendered the analysis of the atoms below this film to be of little value, although he saw a distinct difference (!) between "fresh" and "leached" surfaces. Encouraged by these results, we developed two new reaction cells for leaching our feldspar fragments to prevent contamination by the alleged organic matter. This organic matter could have come from our polyethylene reaction cell, handling the fragments with the fingers, from organic matter in our ion exchange-treated deionized water, etc. (Later we also found that it could have come from oil-diffusion pumps and other sources in Dr. Hercules apparatus.) In any case, we constructed two new reaction cells, one made completely of quartz, and the other completely of teflon. Both cells were scrupulously cleaned

using techniques suggested by Dr. Hercules (washing with hexane, then hot nitric acid). Samples were prepared that were never touched by the fingers, etc. This time we used feldspar cleaved into twin flakes which should have identical compositions. One of the flakes was leached and the other left fresh.

When Dr. Hercules analyzed these flakes, the organic film or residue had been largely eliminated and that problem was solved. Analysis of the various spectra of the samples showed differences, but Dr. Hercules was not able to quantify these differences or explain satisfactorily what they really represented because of his limited experience with this type of sample (an insulator rather than a conductor such as a metal), the differences in chemical composition of the four feldspars, and breakdown of his instrument in the middle of his runs. Also he was unable to obtain the same results on different parts of the same feldspar fragment (perthitic intergrowths?) At this point we realized that each of the three cleavage surfaces of feldspar might also have a different chemical composition on the scale we were looking at, and that crystallographic orientation alone could be causing the apparent differences! Because of these factors, we switched to phlogopite mica.

By splitting a fragment of phlogopite mica, we were certain that the composition of each surface was identical. Again, a leached and a fresh surface were compared by AES. Definite differences were again seen by Dr. Hercules using AES. (Unfortunately, his ISS/SIMS instrument was broken down for more than a year, so we never obtained any results from these methods which should have been more sensitive than ESCA or AES.)

Results of the Auger spectroscopic analyses (AES) are illustrated in figures 5-7, which are the actual spectra obtained from fresh (unleached) and leached phlogopite. Mg, Al, Si, F and O peaks show no recognizable variation in intensity between unleached and leached samples. The K peak intensities, however, do show marked differences. In table III are listed the relative peak heights as measured from these curves. The K:O ratio in the unleached phlogopite was 0.26:1.0. Assuming that the O peak remains constant, the leached phlogopite showed a K:O ratio of 0.052:1.0. Thus, the intensity of the K peak in the leached sample was reduced to about 1/5 that present in the unleached sample. A second set of unleached and leached samples showed almost identical results. These experiments confirm that 1) AES can detect very small changes in K composition on the outer surfaces (10-20^Å deep), and 2) the outer surface of a leached sample is different from that of the fresh sample.

Table III. Relative intensities of potassium and oxygen peaks measured on Auger spectra in figures 5-7.

	<u>I_K peak</u>	<u>I_O peak</u>
Unleached (fresh)	0.26	1.0
Leached	0.052	1.0
(Three months later)		
Unleached	0.24	1.0
Leached	0.125	1.0

Three months after this work was done, these same samples were run again to see if we could detect a difference in composition between basal surfaces and edge surfaces of the leached sample. The purpose was to find if the K released into the solution came mostly from only edges or from basal surfaces or both. Although this question was not resolved, an important finding was made during this study. After standing for three months, the K peak had increased in intensity from 1:5 to 1:2 with respect to the O peak (see figure 5)! This observation was confirmed by analysis of a second leached sample. This is interpreted as a diffusion of K ions from deeper within the structure into positions closer to the surface. One of Dr. Hercules assistants informed us that such observable surface diffusion was common in glasses.

Diffusion in the solid state in crystalline materials is very difficult to observe and is believed to be a very slow process, certainly not likely to be observed in such a short period (3 months). If we have indeed observed diffusion, it should be possible to actually measure the diffusion rate by measuring the change in K intensity over a time period, say a year. It was at this point that we ran out of money for these instrumental analyses. A new grant proposal has been submitted to ARO requesting funds to pursue this diffusion study.

Figure 5. Auger spectrum of fresh (unleached) phlogopite. The K:O ratio of peak intensities is 0.26:1.0.

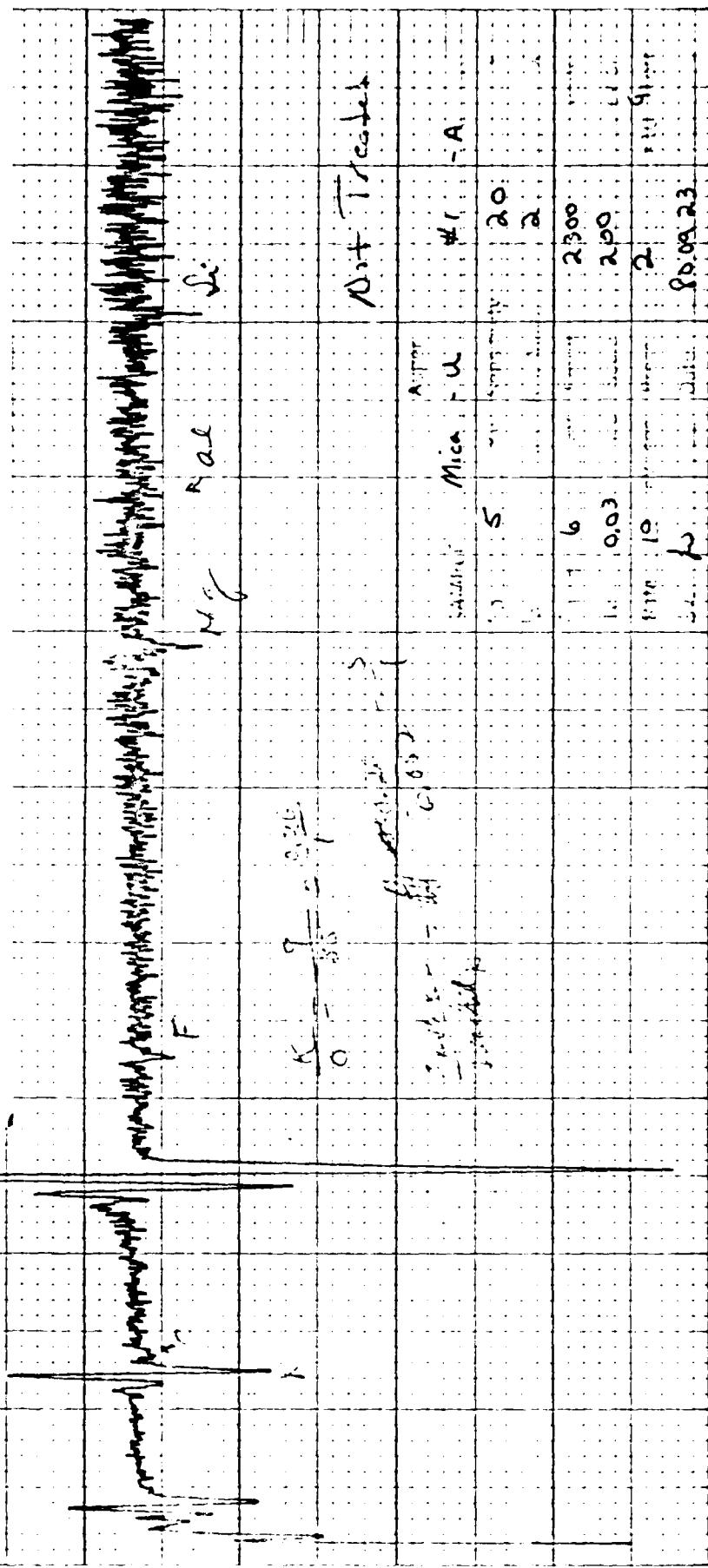


Figure 6. Auger spectrum of leached phlogopite. The K:O ratio is 0.052:1.0.

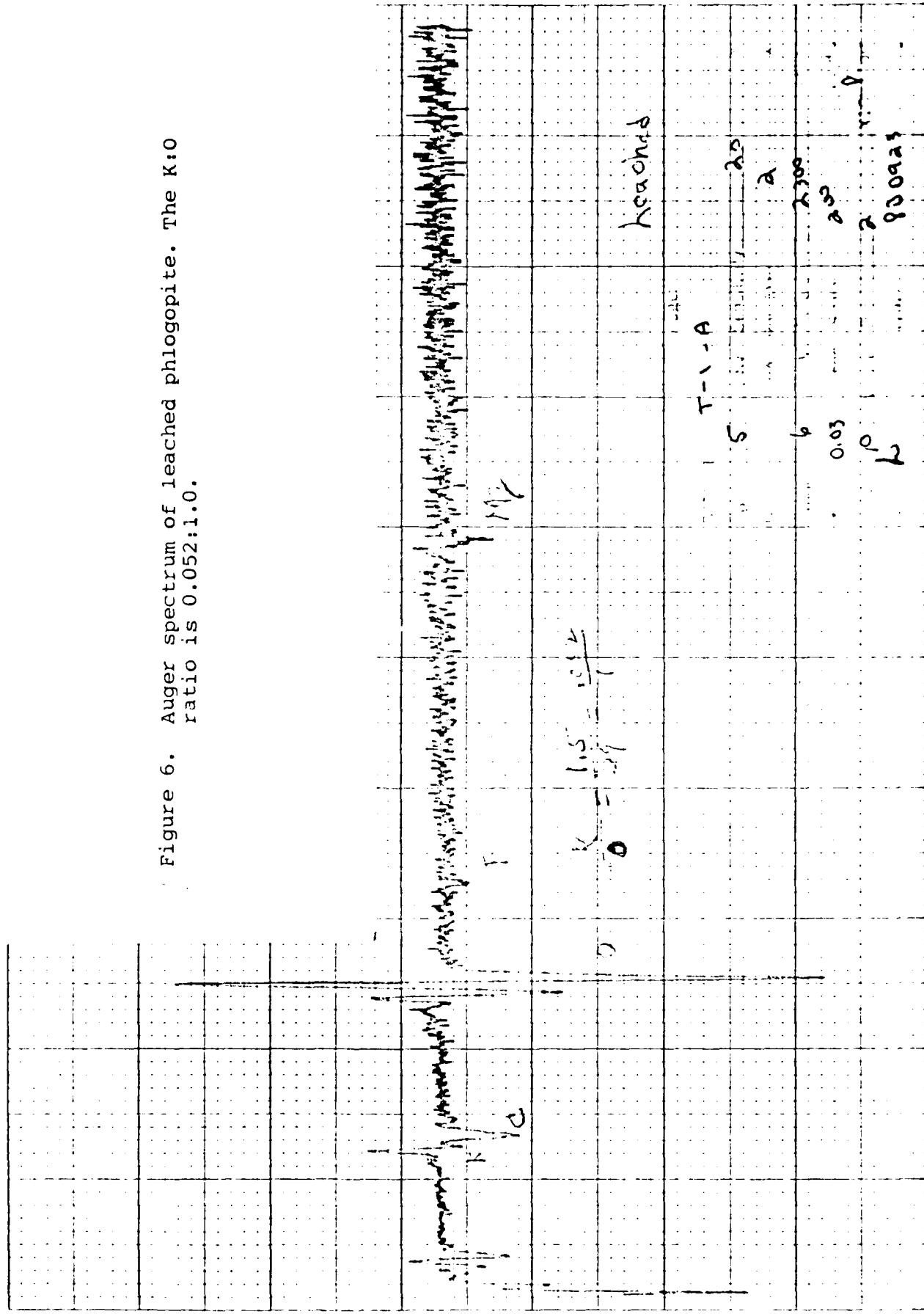
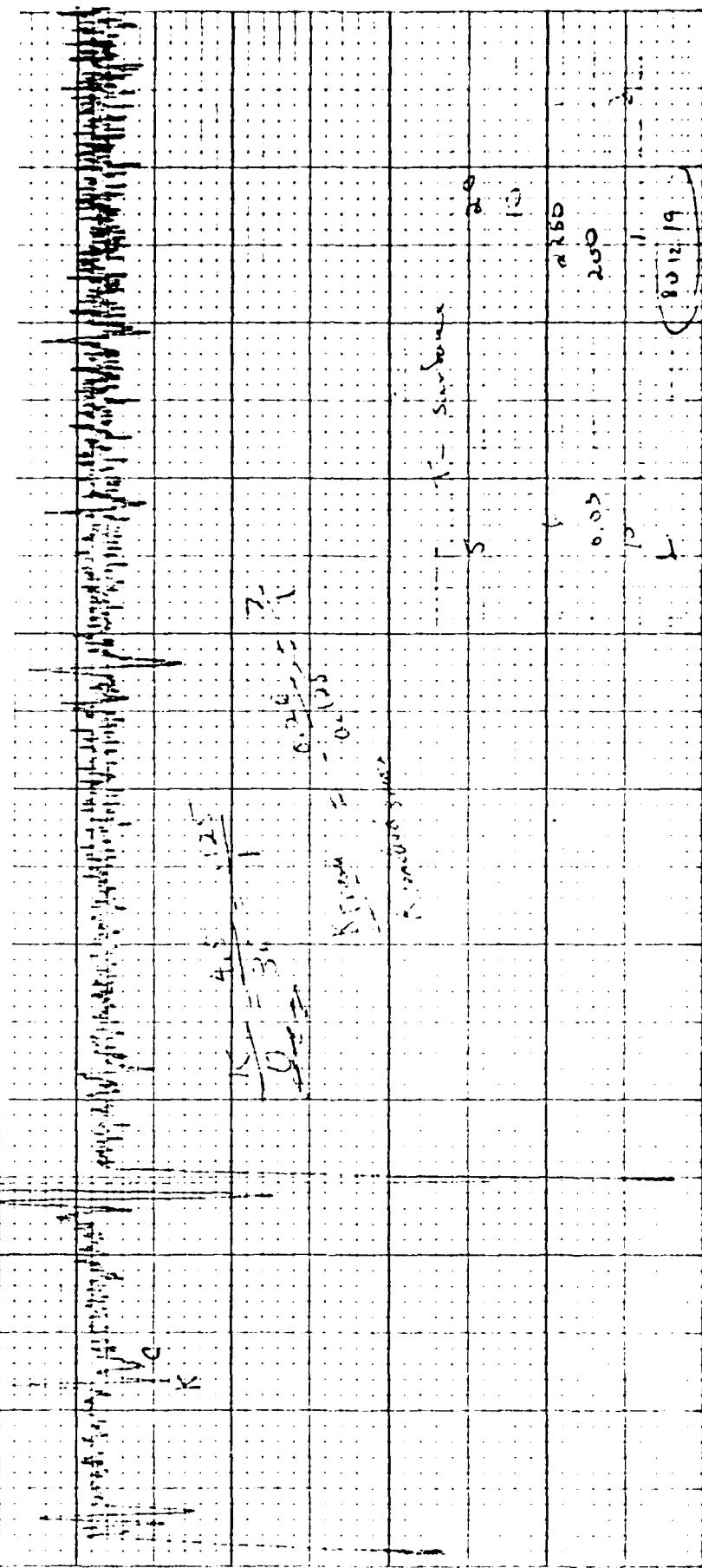


Figure 7. Auger spectrum of leached phlogopite three months after leaching. K:O ratio is 0.125:1.0. A fresh specimen after three months had a K:O ratio of 0.24:1.0, very similar to figure 5.



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